UTILIZATION OF WASTE

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POSSIBLE DIRECTIONS IN RECYCLING CRYSTAL PRODUCTION WASTE

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Methods are proposed for regeneration and subsequent recycling of waste generated in lead crystal production, such as diamond cutting and chemical polishing slime and acid sewage neutralization waste. The specified methods provide for additional economic effects and substantial environmental improvement and make it possible to produce new types of materials (a complex lead-bearing material, low-melting glasses, foam materials).

Environmental aspects have lately become the most topical of technical-economic parameters determining production efficiency, since the protection of atmospheric air and surface and subsurface water from polluting emissions and contaminated industrial sewage has global significance for the future of mankind. At the same time it should be noted that the comprehensive negative per capita effect of the Russian glass industry on the ambient medium is twice the average world level [1]. Environmental problems are especially critical in the production of glassware and ornamental articles made of lead crystal, which requires a stricter compliance with the requirements on decreasing toxic emissions into the air and discharge of contaminant agents into water reservoirs and on recycling of industrial waste [2].

Our study considers some directions of using solid waste of crystal glass production formed at the stage of diamond cutting and chemical polishing.

In diamond cutting of a crystal product a substantial amount of glass is ground off, flushed into the grinding machine sink, and finally transmitted into the industrial sewage system. In our experiments we investigated slime generated in cutting crystal at the Dyat'kovskii Khrustal' Company, which represents powder of a gray-light-blue color compacted in storage. The relative moisture of the slime was 20 – 22%, and the dried material had a bulk density of 760 – 770 kg/m^3 and a specific surface area of 800 – 850 m^2/kg.

The x-ray phase analysis of different batches of glass-cutting slime identified a steady presence of corundum and calcite impurities. Corundum gets into slime during sharpening of diamond wheels and calcite is introduced as a consequence of washing off mark lines made with a chalk suspension.

The processes occurring in heating of slime were studied using thermal treatment in a muffle furnace of briquettes of diameter 20 mm and height 10 mm produced by compression of slime powder. The sequence of the processes is as follows:

500 – 550°C) start of powder sintering;

650°C) formation of a strong sinter with the maximum volume shrinkage;

700°C) vitrification of the surface, the beginning of foaming of the briquette;

750 – 800°C) the maximum increase in briquette volume;

850°C) the beginning of melting of briquettes.

The derivatogram of the glass-cutting slime has a clear exothermic peak (700°C) corresponding to the process of decarbonization of calcite. Apparently, this process leads to intense foaming of the briquettes compressed from the cutting slime. This fact and the high specific surface area of the slime have formed the basis for studying the possibility of producing porous materials, such as foam glass and porous claydite. The obtained foam glass samples have a volume weight of 170 – 175 kg/m^3 and partly communicating porosity. To create a decorative surface in porous claydite tiles, crystal and tinted glass cullet was used together with the slime. The resulting samples of foam glass and porous claydite have radiation-protective properties in contrast to their traditional analogs based on soda-lime glasses.

The introduction of 15 – 20% crystal cutting slime into a household soda-lime glass batch produced a pale blue tint in glass and significantly improved its optical characteristics (refractive index, dispersion, reflection coefficient, and density), Based on the above parameters, the experimental glasses are classified as crystal glasses. The pale blue tint is caused by the presence of elementary copper in the slime, which is contained in the material used as a binder for synthetic diamond grains in grinding wheels. Under oxidizing

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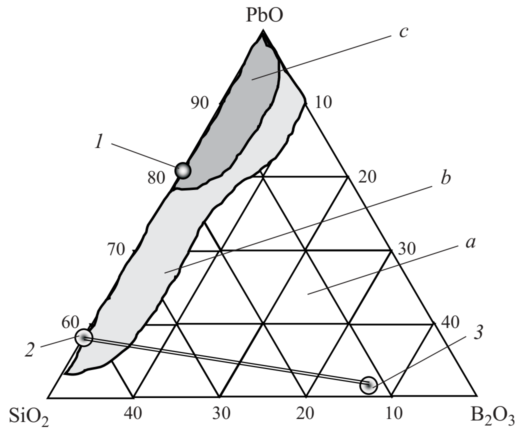


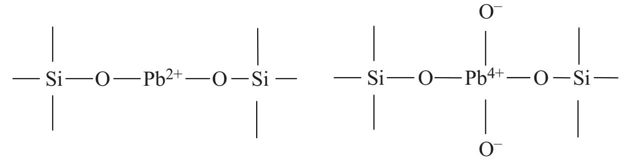
Fig. 1. Glass formation area and position of considered glass compositions in $PbO - B_2O_3 - SiO_2$ system (mol.%): *a*) clear glasses; *b*) glasses crystallizing under heat treatment; *c*) glasses crystallizing in casting; *1*) CLM; *2*) CLM + sand; *3*) CLM + boric acid.

melting conditions the elementary copper transforms into oxide and tints the glass. The melting of batches with slime additives proceeded normally, and the glasses were well melted and clarified under an exposure of 1 h at a temperature of 1420°C. Thus, crystal cutting slime can be used as a pigment for tinting household glasses.

The optimum environmental and technological solution of the utilization of waste generated in the chemical polishing of crystal articles is the separation of the lead-bearing precipitate from acid polishing sewage and subsequent conditioning of each component.

According to the technology developed by us [3], treatment of the lead-bearing precipitate from chemical polishing waste using a sodium carbonate alkaline solution yields the compound $NaPb_2(CO_3)_2(OH)$, which we have named a complex lead-bearing material (CLM). It is proved that the CLM in an amount up to 6 – 10% can be successfully used instead of red lead in lead crystal batches without impairing the quality of crystal glass. Furthermore, the CLM can serve as the basis for low-melting glasses of the $PbO - B_2O_3 - SiO_2$ system.

It is known [4, 5] that lead oxide due to its intense fluxing effect is an indispensable component in low-melting glasses. It is presumed that when the lead oxide content in glass is high, structural groups increasing the degree of cohesion of the glass lattice are formed:



Consequently, the glass formation range in the $PbO - SiO_2$ system includes compositions with molar content up to 80% PbO [5]. It is presumed that lead in glasses with a high molar content of PbO (above 50%) becomes incorporated in the silicon-oxygen lattice, whereas in glasses with a low PbO content (below 30%) lead acts as a modifying ion.

For high-lead glasses of the $PbO - B_2O_3 - SiO_2$ system it is established [4] that $[PbO_4]$ tetrahedra are incorporated in the glass lattice together with $[SiO_4]$ and $[BO_4]$ tetrahedra. With an increasing content of boron and silicon oxides, the continuous lattice of the high-lead glass breaks at the sites of contact of lead with oxygen, since the energy of the Pb – O bond (150.8 kJ) is low compared with the energy of the B – O bond (in four coordination 372.9 kJ) and Si – O bond (444.1 kJ). Consequently, the high-lead glass lattice is preserved at microsites, whereas the bulk of the glass structure consists of $[BO_4]$ groups (with a low content of boron oxide) or $[BO_4]$ and $[BO_3]$ (with molar content of boron oxide over 30%) and $[SiO_4]$ groups. The lead ion in small quantities is present in the lattice interstices as a modifier. In this way the stratification (liquation) of glasses in the $PbO - B_2O_3 - SiO_2$ system takes place.

Figure 1 shows the glass-formation range in the $PbO - B_2O_3 - SiO_2$ system. Compositions with a high content of PbO and a low content of boron and silicon oxides either do not form glasses, or crystallize under heat treatment in the interval of 300 – 600°C.

The point corresponding to the CLM composition on the diagram is located within the range of glasses crystallizing in casting. The CLM was not able to vitrify without additives: the melt crystallized and formed a mixture of yellow and red α-PbO oxides.

The mixture of CLM + sand was well melted at a temperature of 750°C and formed glass upon cooling in air, which was corroborated by x-ray phase analysis.

To produce glasses with low viscosity and surface tension values, boric acid (up to 30 wt.% H_3BO_3) was added to the CLM. The CLM + boric acid mixture was well melted at 700°C with an exposure for 20 min and became vitrified. X-ray phase analysis confirmed the absence of the crystalline phase.

According to the rule of mixtures, the compositions lying on the straight line connecting points *2* and 3 (Fig. 1) are glass-forming as well. Such compositions can be obtained when sand and boric acid are added to the CLM.

Thus, the CLM can be used to obtain low-melting glasses with different parameters satisfying particular service conditions, for instance, enamels for decorating glass or aluminum, low-melting granulated pigments, or glass solders.

A possible direction for recycling the product of neutralization of acid sewage (slime) generated in chemical polishing is the production of gypsum binders [6, 7].

This slime has absolute moisture about 65%. The bulk density of the slime dried and sifted through a No. 08 sieve is 700 – 720 kg/m^3, and its specific surface area is 500 – 510 m^2/kg.

The values of density and specific surface area affect the rate of interaction of gypsum binders with water, setting rate, strength increment rate, final strength, water absorption,

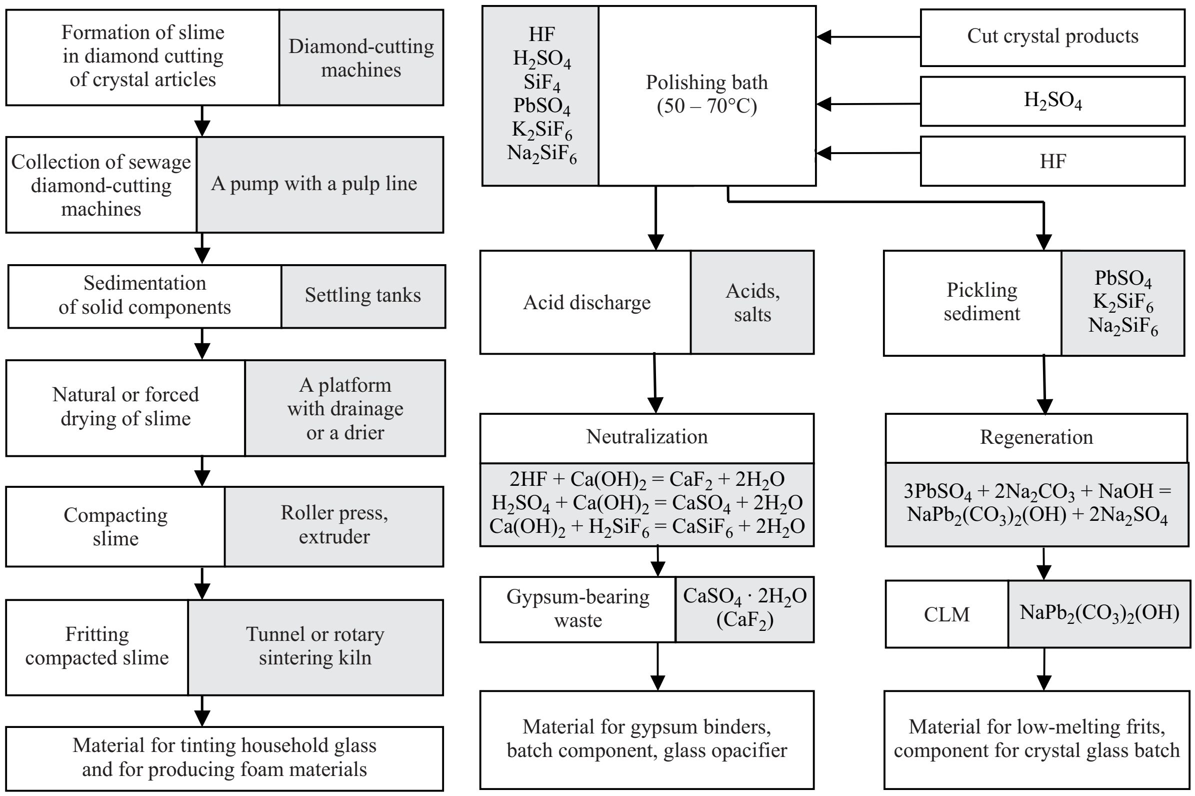


Fig. 2. Technological scheme of conditioning waste from crystal glass production.

packing capacity, and frost resistance. The bulk density of various natural gypsum binders is equal to 800 – 1100 kg/m^3, and the specific surface area of building gypsum is 150 – 200 m^2/kg [6]. As the slime considered is industrial waste, the obtained values can be regarded as satisfactory.

The mineralogical composition of the slime is mainly represented by gypsum dihydrate $CaSO_4 \cdot 2H_2O$. The processing of DTA results revealed that the highest dehydration rate corresponds to the temperature of 155°C, which was selected for thermal treatment of the slime.

The normal thickness of gypsum paste was determined according to GOST 23789–79 and amounted to 66 – 67%. This parameter for building gypsum varies in an interval from 50 to 70%. The setting of material started after 2 – 3 min and ended in 5 – 6 min. Consequently, this binder can be classified as a fast-curing material.

The strength of the standard samples aged 7 days was 1.8 – 2.5 MPa, which corresponds to the parameters of gypsum binders G-2 and G-3 (GOST 125–79).

Slime generated in neutralization can be successfully used as well as glass opacifier, which was corroborated by a prototype industrial production of decorative facing tiles in 1990 at the Pervomaiskii and Neman glass works [8]. The introduction of 3 – 5 wt.% slime from acid sewage neutralization into soda-lime glass batches increases their propensity for consolidation and accelerates the glass-melting process.

The studies performed and the results obtained give reason for proposing an environmentally justifiable scheme for conditioning and further recycling of waste generated in diamond cutting and chemical polishing of crystal glass (Fig. 2).

Today effective solution of environmental problems should be the goal of any production facility.

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